Estimating the Phase Content of Graphite Electrodes from the Electrode Potential^{*}

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INTRODUCTION

Knowledge of the internal state of lithium-ion batteries is crucial for the development of safe optimal charging control algorithms. Most commonly graphite is used as negative electrode, exhibiting high specific capacity and good cycling stability. When such lithium ion batteries are charged, lithium intercalates into the layered carbon structure, and the electrode material transitions through a series of phases differentiated by the number of carbon layers between each lithium layer. Each phase has different electrochemical properties, making it interesting to accurately know the phase content to e.g. guarantee safe charging control. The phase content, however, can only be directly measured through X-ray diffraction experiments, which is not feasible in any battery application. In this work a method based on kernel smoothing is introduced for estimating the phase content of graphite electrodes from the electrode potential, which is readily measurable.

METHODS

The method utilizes the phenomenon where both the evolution of the graphite phases and the electrochemical signals become smoother at higher charging currents (due to the increased phase heterogeinity in the electrode material). The estimation is performed in two main steps, first a reference measurement is performed. In this measurement the battery is charged slowly from a fully discharged state, approximating the open circuit potential of the cell. During the reference measurement, the phase evolution is also monitored using incremental capacity analysis (ICA).

Once the reference phase evolution and electrochemical signal has been gathered, real time phase estimation at a higher current (the target measurement) is possible. This is performed by fitting a Gaussian kernel density function (KDF), such that applying it on the reference measurement results in a smoothing which fits the target electrochemical measurements. Once the KDF is fitted, it can then be applied on the reference phase evolution to estimate the phase content in the target measurement.

Estimating the reference phases

ICA is a commonly used tool for tracking phase transitions during electrochemical cycling (Fly and Chen, 2020),



Fig. 1. Simulated normalized weight fraction of phases during C/60 lithiation (solid lines), plotted together with dx/dU_n curve (dashed lines). It is noted that knee points in the ICA (black squares) coincide with knee points in the phase profile. The resulting reference phase estimation is also shown in the Figure as the dotted weight fraction lines.

as peaks in the IC curve represent phase shifts in the electrode materials. At low rate charging, at most two phases are present in the graphite electrode at a time, and this is also corroborated by our simulations shown in Figure 1, using a reaction limited electrochemical model (Huang et al., 2025). It is also noted that the phase content changes linearly. Assuming that both conditions hold (linear changes, two active phase), then it is sufficient to find the knee points of the phase peaks in Figure 1 to determine the full phase evolution.

Inspectively, it is also observed that the knee points of the IC curve in Figure 1 correspond well in state of charge (SOC, x in $\text{Li}_x \text{C}_6$) to the knee points of the phase peaks. These knee point locations can then provide estimates of the knee points in the phase evolution, and can thus be used to estimate the reference phase evolution. To find the knee point locations, the Bacon and Watts model (Bacon and Watts, 1971) is fitted on each interval between the extreme points of the IC curve. The resulting piece-wise linear phase estimation is shown as dotted lines in Figure 1.

Fitting the kernel density function

Let $(x_R(t), y_R(t))$, $t \in [t_R^i, t_R^f]$ define the measured SOC and the electrode potential from the reference measurement, and let (x_T, y_T) represent the target measurement. The optimization goal is to estimate the phase evolution for the target measurement by smoothing the reference phase evolution $p_R^i(t)$, $t \in [t_R^i, t_R^f]$, where i = 1, ..., 4represents the 4 phases of graphite. This is done by using a truncated Gaussian smoothing kernel

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$$f_{\mu\sigma}(x_R) = \frac{\frac{1}{\sigma}\varphi\left(\frac{x_R-\mu}{\sigma}\right)}{\int_{t_R^i}^{t_R^f}\varphi\left(\frac{x_R(t)-\mu}{\sigma}\right)dt},\tag{1}$$

where σ is the parameter to be fitted, $\mu = x_T$ corresponds to the SOC, and $\varphi(x)$ is the probability density function of the standard normal distribution. The KDF is used to smooth the reference measurement such that the expected value of y_R over f matches the target measurement y_T , i.e. minimizing

$$e_y^2 = (\mathbb{E}_{f_{\mu\sigma}}[y_R] - y_T)^2,$$
 (2)

where $\mathbb{E}_{f_{\mu\sigma}}[\cdot] = \int_{t_R^i}^{t_R^f} [\cdot](t) f_{\mu\sigma}(x_R(t)) dt$. To promote continuity in σ , a forgetting factor $\lambda \in [0, 1]$ is introduced to formulate a constrained recursive least squares problem, which is solved for each new target measurement (x_T, y_T) :

$$\min_{\sigma_T} \sum_{k=1}^n \lambda^{n-k} (\mathbb{E}_{f_{\mu_k \sigma_T}}[y_R] - y_k)^2,$$

s.t. $\sigma_T \ge 0,$ (P)

where *n* is the index of the latest measurement. Once a solution σ_T^* of (P) is found, the estimated weight fraction of each phase *i* is given by $p_T^i = \mathbb{E}_{f_{\mu_T}\sigma_T^*}[p_R^i]$.

RESULTS

Simulated charging of graphite half-cells was performed using the model described in (Huang et al., 2025) for the C-rates C/60, C/40, C/20, C/10, and C/5. The C/60 cycle was used as reference, from which the reference phase evolution was estimated using ICA (shown in Figure 1). The phase evolutions of the remaining cycles were estimated via kernel smoothing of this reference phase evolution. The estimation results are presented in Table 1, with plots of the electrode potential fit for C/5 lithiation shown in Figure 2 and the estimated phase evolution for C/5 lithiation is shown in Figure 3. This shows that the estimation error remains low for all currents tested, and while the error increases for the higher C-rate lithiation, the phase estimation error remains lower than the reference phase estimation error. From Table 1 it can also be seen that the fitted standard deviation σ increases for higher Crates, this represents an increased inhomogeneity at higher currents.

DISCUSSION

The findings indicate that kernel smoothing is a viable technique for estimating the phase content within a graphite half-cell from the negative electrode potential, underscoring the method's potential applicability. It is recommended that future research should apply this method on full battery cells, which include a positive electrode component. The graphite electrode phase transitions could remain dominant in the electrochemical signals, depending on the electrode material utilized. This would permit the application of the estimation method, albeit with an increased estimation uncertainty. Given that critical degradation phenomena, such as lithium-plating, depend on the internal states of the battery, integrating phase estimation into battery management systems may enhance the safety of fast charging applications.



Fig. 2. Plot of fitting accuracy, showing the reference (blue), the target (red) and the smoothed (yellow) negative electrode potential. The smoothed potential is found by applying the fitted KDF on the reference potential, and it is plotted together with 68% confidence bounds ($\pm 1\sigma$).



- Fig. 3. Comparison of estimated phase fractions (dotted lines) and ground truth phase fractions (solid lines) for simulated C/5 lithiation of a graphite half-cell.
 - Table 1. Mean of fitted σ_T , mean squared errors (MSE) of curve fit (y_T) , and phase prediction (p_T) , for different C-rates. Also included is the MSE of the reference phase estimation. MSE is given in terms of 10^{-4} .

C-rate	$Mean(\sigma_T)$	MSE y_T	MSE p_T
Ref	-	-	8.3
C/40	0.0022	0.395	5.45
C/20	0.0022	0.440	5.35
C/10	0.0093	0.453	4.43
C/5	0.0172	0.412	7.07

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